

MEASUREMENT OF THE DENSITY OF HIDE AND LEATHER*

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ABSTRACT

The density gradient technique, a relatively simple method for measuring the real density of hide and leather, is described. The preparation and calibration of the density gradient columns are also given. Densities obtained by this technique for several differently processed hides are reported. The effect of sorbed water on density is shown for three leathers.



INTRODUCTION

A relatively simple, versatile, rapid, and inexpensive method for accurately measuring the real density of solids, powders, fibers, and even liquids is the density gradient technique (1). This technique has been applied in the study of cotton (2), plastics (3), wool (4), and other proteins. It is an approved ASTM standard test method (5) for plastics. The possibility of using the method for routine determination of the density of hide specimens is apparent.

An examination of the hide and leather literature revealed no reference to the density gradient technique, although numerous other density-measuring techniques had been employed and discussed (6, 7, 8). These techniques often required a considerable amount of a researcher's time and in some cases were complicated (7, 8). Therefore, an investigation of the density gradient technique was made to determine the suitability of the method for routine use with hide and leather.

The present investigation describes the use of the density gradient column for the determination of density on a variety of light leathers and includes the preparation and calibration of gradient columns.

EXPERIMENTAL

The principle of the gradient column is quite simple. By mixing liquids of different densities in varying ratios a density gradient column can be produced

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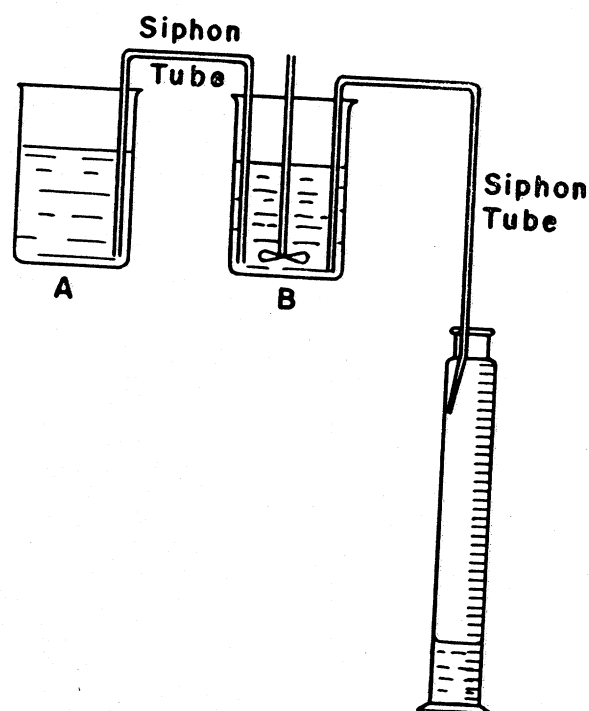


FIGURE 1.—Apparatus for gradient preparation.

complished by introducing small droplets of aqueous salt solutions of varying densities. On the other hand, if the gradient is composed of aqueous salt solutions, various organic liquids of known density can be used. An alternate method, and the one employed in the present work, is to use glass floats of known densities. These floats are commercially available. The glass floats used were calibrated and accurate to $\pm .0001$ g/ml.

The standard glass floats having densities in the range of the column were placed in the column, and their "rest" position was noted. The exact position of each float is read from the scale of the column or from a millimeter rule supported against the side of the column. The density at any point in the gradient column is obtained by plotting the density of the standard floats against their column position. Shown in Fig. 2 is a typical calibration curve obtained from carbon tetrachloride and toluene mixtures. The plot is essentially linear over the density range 1.300 to 1.450 g/ml. Densities could be determined from the specimen position to $\pm .001$ g/ml without any difficulty. The sensitivity of such columns depends, of course, on the density difference of the two liquid components and can be adjusted as desired. A column with a sensitivity of about .001 g/ml was considered more than adequate for illustrating its utility with hide and leather specimens. In order for such a column to be of practical importance

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that will show an essentially linear variation in density with respect to position within a column. A sample suspended within the liquid column comes to rest at that position which corresponds to its own density.

In order to prepare a column two miscible liquids are generally selected so that the desired density range is obtained. The sensitivity of the column produced depends upon the difference in density between the two liquid components. For substances with unknown densities, a wide-range column is used as a survey. Once the desired range is established, a second column is prepared to increase the accuracy with which the density can be measured. The liquids chosen may be organic compounds or aqueous salt solutions. Those selected depend upon the substance being studied and the density range required. Caution must be exercised in selecting the liquid components, as it is essential that there be no interaction between column components and substances being studied. The two liquid components that were found suitable for hide and many leather specimens were toluene and carbon tetrachloride. The density range covered in the survey column for leather was 1.10 to 1.59; in the more sensitive columns it was from about 1.30 to 1.40. Three of the sensitive columns were prepared and maintained under different temperature conditions as follows: (a) room temperature which varied about $\pm 4.0^{\circ}\text{C.}$, (b) in a constant temperature room at $23^{\circ}\text{C.} \pm 1^{\circ}$, and (c) in a constant temperature bath at $25^{\circ} \pm 0.1^{\circ}$. In addition, a sensitive toluene-bromobenzene column and a silicone-carbon tetrachloride column maintained in a constant temperature room at 25°C. were employed as a check for interaction of the column components with the materials being studied.

Gradient columns can be prepared in a number of ways. The method that was used in the present study is illustrated in Fig. 1. The apparatus consists of two beakers of the same size connected by means of a siphon. The beaker labeled B contained the heavier liquid; the beaker labeled A, the lighter liquid. Beaker B is connected by means of a siphon to an appropriate cylinder. Glass-stoppered graduates with a capacity of 300 ml. were found quite adequate for making gradient columns. The siphon used to deliver the liquid to the column should have a fine capillary tip which is in contact with the side of the cylinder. This will keep mixing at a minimum when the cylinder is being filled. Beaker B is equipped with a stirrer. Its purpose is to mix the incoming, less-dense liquid with the more-dense liquid already contained therein. After the system is primed, the delivery of liquid to the graduated cylinder is started. It is obvious that the system is delivering a gradually decreasing density mixture to the graduate. Initially there is being delivered to the receiver a much greater proportion by volume of the dense liquid; finally, the reverse is true. Through the application of this procedure it is possible to establish a very nearly linear gradient in the cylinder.

Calibration of the established gradient column can be carried out in a number of ways. If the gradient is composed of organic components, calibration is ac-

to remove all entrained gas. This is accomplished by either applying a vacuum during the "wetting out" process or by mechanically working the specimen. Application of repeated pressure of a glass rod worked quite satisfactorily on light leather specimens. Specimen size is not important for homogeneous materials. The smaller the size the greater the ease of reading its position in the column. For convenience, specimens of various shapes were used for identification purposes, as a number of specimens were studied simultaneously. Maximum specimen dimension was about 1 cm.

After "wetting out" and removal of entrained gas, the leather specimens were placed in the gradient column, and their movement as a function of time was observed. A number of samples were studied, and the time to reach equilibrium was determined. To insure that equilibrium had been attained, the final density was recorded at 24 hours. All samples had been equilibrated for months in an atmosphere of 50% R.H. and 23°C.

Three specimens were cut from the same area of the hide to minimize variations. Several specimens were ground, and the densities of the fibers were measured. In addition, a study was made of the change in the density produced by varying the amount of sorbed water contained by the skin. The samples were first dried in a vacuum oven at 50°C. for 18 hours and then placed in a vacuum desiccator over water and allowed to pick up water. Samples were removed at various levels of uptake, and their densities were determined.

As a check on the density gradient method, density measurements were also made using the pycnometer method for several of the materials studied, using toluene, kerosene, and silicone fluid as the displacement mediums.

RESULTS

Shown in Fig. 3 is the change with time in the density gradient column containing toluene-carbon tetrachloride for two light leathers. Approximately 100 minutes are required for the specimens to approach an equilibrium position. The position of the chrome-vegetable calf specimen was the same at the end of 24 hours as it was at 100 minutes. However, the vegetable-tanned calf specimen after 24 hours showed a slightly lower position. This position corresponds to a slightly greater density, but the increase was only about .003 g/ml. Up to the present time we have investigated over 20 different types of leather specimens and found that the greatest increase in density after 100 minutes was .009 g/ml. Generally it was much less. In a few instances the 24-hour observation showed a very slight decrease in density, about .003 g/ml.

The change in density after 100-minute observations could be due to an equilibration of medium and the fibrous network of the leather specimen. The change could also be due to extraction by column medium of some components of the leather such as fatliquor or tanning agent. Measurements made with column

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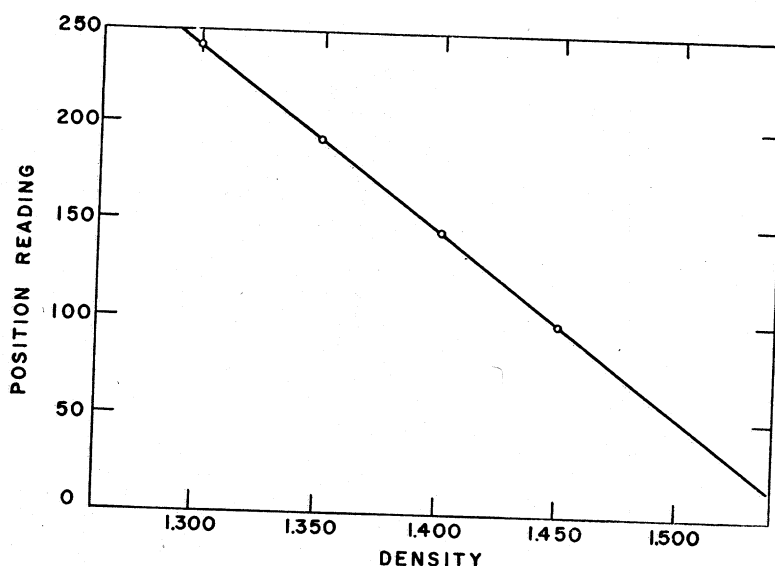


FIGURE 2.—Typical calibration curve for a density gradient column.

in addition to accurately measuring density it should be stable for long periods of time. Columns of this type if maintained in a constant-temperature bath to $\pm 0.1^\circ\text{C}$. will remain unchanged for months. Although it is not generally realized, the process of diffusion is quite slow in such columns. In a constant-temperature room maintained to $\pm 1^\circ\text{C}$., little change in a gradient column was observed over a period of two months. Perhaps of even greater interest is the result of our observations on a gradient column standing in one of our laboratory rooms for about 1 month. The temperature of the room fluctuated from 23° to 28°C . over this period. The gradient column had a density range from about 1.25 to 1.50. Readings of the positions of five floats were made daily at about 26°C . over the period of four weeks. The change in density in the center of the column at the end of this period was only 0.002. The extreme ends of the gradient column showed no detectable change until 8 days had elapsed. After this period the density gradually increased or decreased producing a non-linearity in the density of the column. However, even at the end of four weeks the column was suitable for density determination as long as the calibration curve of that date was employed. It should be pointed out that specimens can be removed from the column without any apparent change to the gradient if it is carried out with care. This can be accomplished quite easily by slowly lowering a small, fine-meshed cup attached to a thin wire into the gradient and slowly withdrawing it.

The procedure that is generally followed in making a density measurement on a solid is to "wet" the specimen with the less-dense liquid of the column before placing it into the column. For fibrous materials, including leather, it is necessary

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TABLE I
DENSITY OF LIGHT LEATHERS

Leather	Moisture %	Density			Avg.
		Gradient Column			
		1*	2†	3‡	
Calf; enzyme-unhaired, washed, acetone-dehydrated	18.5	1.326	1.319	1.325	1.323
Calf; limed, bated, washed, dehydrated	19.2	1.333	1.333	1.338	1.335
Hide; veg.-tan, chrome-re- tan, unfinished, upholstery	10.4	1.356	1.343	1.352	1.350
Hide; veg.-tan, chrome-retan, finished, upholstery	11.2	1.352	1.355	1.359	1.355
Side; chrome-tan, resorcinol- formaldehyde retan, unfinished	15.6	1.351	1.348	1.347	1.349
Side; double chrome-veg. retan, mechanical	14.2		1.436		
Side; glutaraldehyde-tan	15.8		1.308		
Calf; veg-tan, unfinished	14.0		1.382		

*25°C. bath

†23°C. constant-temperature room

‡Room temperature

curate density, and the removal of entrained air even under a vacuum of .05 mm. Hg was extremely difficult. Reproducible results were obtained which showed no essential difference between media; however, the "density" value depended upon the method of sample preparation, e.g., using strips, cubes, or ground fibers and house vacuum or a vacuum pump. For example, the largest pycnometer density obtained in kerosene for a vegetable-tanned, chrome-retanned, unfinished upholstery specimen was 1.310 g/ml, compared with a value of 1.35 g/ml by density gradient technique. This specimen contained 10.4% water and was deaerated at .05 mm. Hg for 1 hour in the form of strips.

The effect of sorbed water on density is shown in Fig. 4 for two leathers and an untanned calfskin. Each sample exhibited a somewhat different density change with increasing water content. The effect of increasing water content on a vegetable-tanned, unfinished calf skin leather showed a constant, nearly linear, decrease in density up to 32% water content, the maximum studied. The total decrease was .03 g/ml. A chrome-tanned resorcinol-formaldehyde-retanned, unfinished side leather also showed a continually decreasing density with increased water content. However, it differs from a vegetable-tanned, unfinished calf spe-

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media other than toluene and carbon tetrachloride gave the same results within the limits of experimental error. Two such columns contained toluene-bromobenzene and silicone-carbon tetrachloride. However, whether the 24-hour density value or 100-minute density value is used is immaterial, since the difference in the two densities is so small and within the variation encountered for adjacent samples.

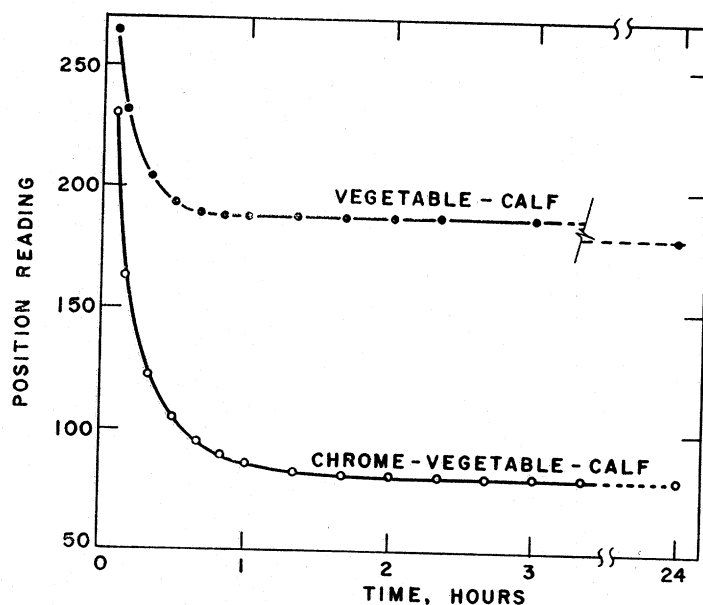


FIGURE 3.—Typical curves showing change in column position with time for two different leather samples.

Shown in Table I are the measured densities obtained by density gradient for eight hides which have all received different processing treatment. The densities were those recorded after 24 hours for three gradient columns and are the average of three samples in each column. The maximum variation in density observed for any three samples was $\pm .006$ g/ml. The average variation for the three columns was only $\pm .004$ g/ml. It can be seen that, in general, there is good agreement with little difference between the three columns, even though the columns were subjected to different temperature conditions. The densities observed for several ground-leather samples were the same as found for the unground pieces, provided a representative sample was used. If entrapped air were responsible in part for the measured density of whole pieces of leather, then it would be unlikely that the agreement observed would have been attained.

It was found that it was extremely difficult to obtain an accurate density using a pycnometer because a large sample of material is needed to obtain ac-

ever, the meaning of density as obtained by this method has not been considered. The term density (mass per unit volume) is a macroscopic concept. As pointed out by Hermans *et al.* (9) the macroscopic concept loses its physical meaning if the medium employed can penetrate into the molecular structure, that is, occupy positions within molecular holes. The molecules of the medium, therefore, must be large compared with these molecular dimensions. Helium, for example, is known to penetrate through cellulose films and many other substances. It is obvious that helium could not be used to evaluate the true or real density of such substances. Such measured densities would be greater than their true densities.

In order to obtain a true density for leather, the molecules of the medium employed must be larger than the molecular spaces between the collagen helices or the available molecular space associated with the helix itself. Pomeroy and Mitton (6) showed that gas media such as air, nitrogen, and hydrogen give rise to densities for leathers that are too high. Penetration into the molecular structure of leather takes place which is accompanied by some sorption. Helium gave somewhat lower values than the other gases. Even though penetration into molecular holes is possible, it is quite unlikely that helium would be sorbed. However, as shown in reference (6), the density value obtained with helium is about 4% greater than that obtained with various inert liquid media. These results indicate that a liquid medium composed of molecules that are somewhat larger than the gases discussed and relatively nonpolar in character would be most suitable for measuring the real density of leather. Therefore, the density gradient technique as employed in this study, which uses nonpolar molecules that are larger than the gases cited, should fulfill the requirements necessary for measuring the real density of leather.

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